(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 737 510 A2

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
16.10.1996 Bulletin 1996/42

(51) Int. Cl.^{6}: **B01J 3/06**

(21) Application number: **96105789.0**

(22) Date of filing: **12.04.1996**

(84) Designated Contracting States:
DE IE

(30) Priority: **13.04.1995 JP 113784/95**
07.02.1996 JP 46603/96

(71) Applicant: **SUMITOMO ELECTRIC INDUSTRIES, LTD.**
Osaka-shi, Osaka 541 (JP)

(72) Inventors:
- **Degawa, Junji,**
  c/o Itami Works of Sumitomo
  Itami-shi, Hyogo (JP)
- **Tsuji, Kazuwo,**
  c/o Itami Works of Sumitomo
  Itami-shi, Hyogo (JP)
- **Fujioka, Akifumi,**
  c/o Itami Works of Sumitomo
  Itami-shi, Hyogo (JP)
- **Goda, Yasushi,**
  c/o Itami Works of Sumitomo
  Itami-shi, Hyogo (JP)

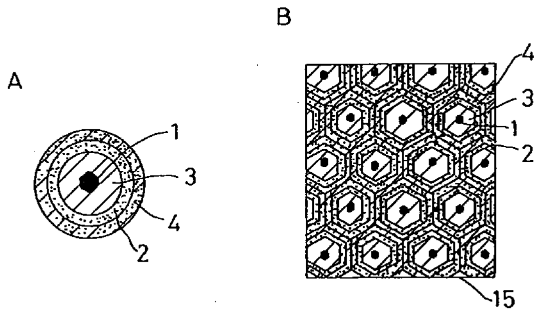
(74) Representative: **Kindler, Matthias, Dr. Dipl.-Chem. et al**
Hoffmann, Eitle & Partner,
Patent- und Rechtsanwälte,
Arabellastrasse 4
81925 München (DE)

(54) Coated particles for synthesizing diamond and process for production of diamond abrasive for sawing

(57) A coated particle for synthesizing diamond comprises; a single crystal of fine diamond particle (1) being coated with at least one layer (2) which contains at least one kind of solvent metal powder for synthesizing diamond and/or at least one kind of solvent metal powder with organic bonding material.

Diamond abrasive particles for sawing are produced by a process which comprises steps of : coating fine diamond particles (1) with at least one layer (2) which contains at least one kind of solvent metal powder for synthesizing diamond and/or at least one kind of solvent metal powder with organic bonding material, filling a molding with said coated fine diamond particles, compacting, arranging a compact in a synthesizing vessel, heating said compact to a temperature above a solvent metal-graphite melting point with a pressure condition in which diamond is thermodynamically stable, and recovering said diamond abrasive particles.

Fig.2



Printed by Rank Xerox (UK) Business Services
2.13.8/3.4

Description

BACKGROUND OF THE INVENTION

(1) Field of the Invention

The present invention relates to a single crystal diamond particle having 20~60 U.S. mesh (hereafter mesh means U.S. mesh) and the method of making the diamond particle. The diamond particle is used as an abrasive for sawing, especially to cut stone, concrete and asphalt.

(2) Description of the Prior Art

Because stone, concrete and asphalt are hard and brittle materials, the diamond particle which is used as an abrasive for sawing to cut the above materials, is required to be high-strength and not friable. There is a strong mutual relationship between cutting performance (tool life) and particle strength. And it is well known that the particle strength depends on the perfection and symmetry of the diamond particle shape.

When there is a lack portion 29 (broken or not grown portion) at the surface of a diamond particle 28 as shown in Fig. 11A, strength of the particle decreases depending on the extent of the lack portion. Fig. 11 B shows a long and narrow diamond particle 30 and a sharp-edged diamond particle 30. Such diamond particles have low strength due to lack of symmetry. A high-strength diamond particle is required to have no or minimal lack portion and good symmetry.

The environment of a growing diamond cause a lack portion or poor symmetry of a grown diamond. When growing diamonds have insufficient distance, the growing diamonds contact each other or are unnaturally restricted, even though not contacting, by supply of raw material and the surroundings. For these reasons, many synthesized diamond particles have a lack portion and bad symmetry. Therefore, it is necessary to have sufficient distance between growing diamonds for synthesizing high-strength diamond.

However, the sufficient distance is contrary to ecconomical demand which is to grow as many diamond particles as possible in a limited-space synthesizing vessel. It is required industrially to grow diamonds as densely as possible, maintaining the lowest necessary distance between the grown particles.

On the other hand, there are generally two methods of synthesizing a diamond particle.

The first method as shown in Fig. 12A, is that a compact ("compact" is defined as a powder or particle compacted in a die or mold) of mixture which is raw material of non-diamond carbon powder (usually graphite and hereafter written as "raw carbon") and solvent metal powder (usually a combination of Fe, Co, Ni, Cr and Mn and hereafter written as "solvent metal") for diamond synthesizing, is maintained at a thermodynamically stable region of diamond and above the melting point temperature of metal-graphite (usually 5~6 GPa and 1300~1600°C). (This method is hereafter written as "powder method.")

The second method as shown in Fig.12 B, is that a multilayer of raw carbon plates 7 and solvent metal plates 6 is maintained at a thermodynamically stable region of diamond and over the melting point temperature of metal-graphite the same as the powder method. (This method is hereafter written as "multilayer method.")

Comparing these two methods, it is thought that the powder method is superior to the multilayer method in terms of yield since the three-dimensional space of the synthesizing vessel is effectively used, and the multilayer method is superior to the powder method in terms of strength of diamond particles since interference between synthesized diamond particles is limited in one plane.

For effective manufacturing of intended particle size diamond in these two methods, fine single-crystal diamond particles are dispersed as seed crystals in the mixture or in the solvent metal plate. In this case, diamond particles are synthesized around the seed crystals. However, since simply dispersing seed crystals are indispensable for uniformless dispersion in the mixture or in the solvent metal plate, the synthesized diamond particles are also indispensable for dense and rough arrangement.

A diamond particle is synthesized to larger than the intended particle size at the roughly arranged portion and many diamond particles have a lack portion and poor symmetry because of interference at the densely arranged portion.

The multilayer method is proposed and practically used in that the seed crystals 1 are arranged regularly in the solvent metal plate 6 as shown in Fig. 13 to resolve the issue (for example Tokko-shou 63-57099, corresponding U.S. Pat. No. 4,547,257and Tokkai-hei 5-23574, corresponding U.S. Pat No. 5,194,070). This method results in higher-strength and higher yield ratio of the intended diamond particle size than previous techniques. The seed crystals are arranged ideally in a plane, but the yield is insufficient since there is useless space in the vertical direction. The seed crystals are isolated by only the liquid phase of solvent metal under the synthesized condition of diamond, therefore the arrangement sometimes results in rough and dense portions of diamonds because of movement of the seed crystals.

SUMMARY OF THE INVENTION

It is, therefore, an object of the present invention to provide a particle for synthesizing diamond, comprising a single crystal of fine diamond particle being coated with at least one layer which contains at least one kind of solvent metal powder for synthesizing diamond and/or at least one kind of solvent metal powder with organic bonding material.

It is preferable that said layer includes non-diamond carbon.

It is preferable to use acrylic copolymer as the organic bonding material.

The object of the presnt invention is achieved by a process for the production of a diamond abrasive for sawing, comprising the following steps: coating fine diamond particles with at least one layer which contains at least one kind of solvent metal powder for synthesizing diamond and/or at least one kind of solvent metal powder with organic bonding material, filling a molding with said coated fine diamond particles ,compacting, arranging a compact in a synthesizing vessel, heating said compact to a temperature above a solvent metal-graphite melting point with a pressure condition in which diamond is thermodynamically stable, and recovering said diamond abrasive particles. It is preferable to coat the fine diamond particles by spraying method, especially by Wurster type fluidized bed or horizontaly rotating disk equipment.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 A shows a schematic cross section of a coated diamond particle used in the Examples.

Fig. 1 B shows a schematic cross section of a coMPact used in the Example.

Figs. 2 A and B show schematic cross section of other embodiments of this invention the same as Figs. 1 A and B.

Fig. 3 shows a schematic cross section of other embodiments of a coMPact used for synthesizing diamond.

Fig. 4 shows other embodiments of a coMPact the same as Fig. 3.

Fig. 5 A shows a schematic cross section of a compact in which coated particles are compacted in a mono-layer.

Fig. 5 B shows a schematic cross section of the mono-layer coMPact stacked with other fillers in a synthesizing vessel.

Fig. 6 A schematic showing a method of coating with sprayed powder in a fluidized bed.

Fig. 6 B schematically showing a method of coating with sprayed powder on a horizontally rotating disk.

Fig. 7 A schematic showing Wurster type fluidized bed with an inner cylinder.

Fig. 7 B schematic showing Wurster type fluidized bed with broder portion at upper parts.

Fig. 8 A schematic showing a wet-cold-isostatic-press.

Fig. 8 B schematic showing a dry-cold-isostatic-press.

Fig. 9 A schematic showing an example of a supporting case, Fig. 9 B showing another example.

Fig. 10 A schematic showing a one-axis type.

Fig. 10 B schematic showing a multi-axes type of ultra-high pressure apparatus for synthesizing diamond.

Fig. 11 A schematic showing diamond particles having a lack portion.

Fig. 11 B schematic showing diamond particles having poor symmetry.

Figs. 12 A and B show prior art arrangements of powder method and multilayer method in synthesizing vessels.

Fig. 13 shows another prior art arrangement in synthesizing vessels, namely, regularly arranged seed crystals in multilayer.

Fig. 14 shows a schematic cross section of steel capsule for measuring impact strength.

DETAILED DESCRIPTION OF THE INVENTION

The present inventors have considered to solve the above issues, and have focused on the method of using compacted raw material which is made from each fine seed crystal (fine single crystal diamond) being coated with sufficient amounts of raw carbon powder and solvent metal powder. Sufficient amount means that the coated seed crystals are large enough so that grown diamond particles do not contact each other. Therefore, it is fundamentally required that the coated seed crystals are larger than the intended synthesized diamond partilces.

Further study on the following is required for practical use:

(1) Pore in the coated seed crystals

When the coated crystals are compacted, the pore in the coated crystals is broken and the distance between the seed crystals decreases.

(2) Open space among the seed crystals in a mold or a die.

When the coated seed crystals are compacted in a mold or die , the open space among the seed crystals decreases.

(3) Compaction of non-uniformity

Distance between each seed crystal decreases in only one specific direction in some methods of compaction.

(4) Remaining pore in a compact

Since the pore is broken under the synthetic condition of diamond, the distance between the seed crystals decreases.

(5) Since the volume of raw carbon decreases when the raw carbon changes to a diamond.

Therefore the size of the coated seed crystal is far larger than the intended synthesized diamond particles.

After many experiments on practical manufacturing methods of coated seed crystals, the present inventors have invented this method to coat the seed crystals with raw carbon powder and solvent metal powder.

According to the present invention:

(1) The distance between the seed crystals can be controlled by the thickness of the coated layer (size of coated seed crystals), pore ratio in the coated layer and selection of compaction methods.
(2) The yield amount of diamond increases since the compact of coated seed crystals can use the synthesizing vessel three-dimensionally and effectively.
(3) Each seed crystal does not move since each seed crystal is isolated by a solid material of raw carbon under the condition of synthesizing diamond.

Therefore, this invention remarkably improves the yield amount and strength of diamond coMPared with prior arts. The most fundamental constitution of this invention is comprised of using a compact 15, as shown in Fig. 1 B of fine seed crystals 1 coated with the mixture of raw carbon powder and solvent metal powder, as shown in Fig. 1 A. The same results can be obtained in using the coMPact 15, as shown in Fig. 2 B of fine seed crystals 1 coated with solvent metal layer 3, mixture layer 2 and a carbon layer 4 as shown in Fig. 2 A. It is essential that the coated layer includes raw carbon and solvent metal. But solely raw carbon is not preferable for the innermost layer, because the seed crystals grow large with their change from carbon to diamond, namely through solvent metal. The second and outer layers are optionally selected. For example, multilayer coated seed crystals such as, seed crystal/solvent metal/raw carbon/solvent metal/ raw carbon, or seed crystal/solvent metal/mixture of raw carbon and solvent metal/raw carbon, can also be used. Moreover, each layer can be changed to different mixture ratios of raw carbon and solvent metal and different kinds of solvent metals.

Also, the compacted mixture of these coated crystals, raw carbon powder and / or solvent metal powder, is industrially available. It is possible to decrease the amount of the coated material as much as the mixed amount of the raw carbon powder and / or the solvent metal powder. But it is indispensable in this method, as shown in Fig. 3 that there are contacting and not contacting areas between the coated particles depending on the condition of the added powder 5. Distances between the seed crystals vary in proportion to the added powder. When powder is added too much (the coated amount is too little), there is little improvement coMPared with the powder method. In assessing the advantage of the present invention, therefore, the true volume of the coated particles (the amount of seed crystals, raw carbon and solvent metal excluding pore and organic bonding material) must be at least 20 volume %. When the mixed powder includes raw carbon in this method, it is not necessary to include raw carbon in the coated particles.

The thickness and composition of the coated layer and the amount and composition of the mixed powder, needless to say, are determined by considering the intended diamond particle size, distance between seed crystals, amount of raw carbon and solvent metal, compaction method and deformation of compact at synthesized condition of diamond in all of the above methods. Seed crystals, raw carbon and solvent metal which are used in the present invention, are the same as those used in the prior technique. The seed crystal is usually in the range of 10~200 μm diameter since large seed crystal is liable to contain inclusions (impurities): seed crystal is preferably very fine because it handles easily. When a seed crystal is too small, it is difficult to handle. But seed crystal should be single crystal. Any usual graphite can be used as raw carbon. The combination of Fe, Co, Ni, Cr and Mn (each material, alloy or mixture) which are used in the prior technique, can also be used as solvent metal.

The invented producing methods which are explained in detail hereafter, are related to producing coated particle and compact using the coated particle.

The producing methods of coated particle are explained first. To obtain an advantage of this invention, fundamentally any method can be used provided that each seed crystal is coated uniformly. The methods such as plating method, chemical vapor deposition method, coating with sprayed powder method, mechanical alloying method, etc., are considered for use in this invention.

However, there are disadvantages in the chemical reaction methods such as the plating method and chemical vapor deposition method, because raw materials are expensive and there are difficulties in thick coating and in the coating mixture with raw carbon. Therefore, there are advantages in the coating powder methods such as the coating with sprayed powder method and mechanical alloying method because there is no drawback as in the chemical reaction method. Organic bonding materials can be used in the coating with powder methods. Because organic bonding materials can be removed easily by heat treatment after the coating. Moreover, it is sometimes preferable that an overabundance of organic bonding material be intentionally added, in adjusting the ratio of distance between seed crystals in the compact as described later.

According to the many experiments that were carried out by the present inventors, the coated with sprayed powder method was the simplest, easiest and most cost-efficient method. This method has been widely used in the field of producing pharmacies and foods. This method is carried out by spraying the mixture of solvent metal powder, raw carbon powder, organic bonding material and organic solvent from the spraying nozzle 10 to the fine single crystal diamonds 1 or semi-coated single crystal diamonds (hereafter defined as "core particle") as shown in Fig. 6A in which a core particle is fluidized or as shown in Fig. 6B in which a core particle is stirring. In the figures, 9 is the outer cylinder of the coating equipment, 11 is porous plate, 12 is horizontally rotating disk, 13 is supply tube for powder, (a) is flow of slurry which contains powder to be coated/organic bonding material/organic solvent, (b) is flow of organic bonding material/organic solvent, (c) is flow of powder to be coated , (d) is flow of gas to dry the coated powder and (e) shows rotating direction of horizontally rotating disk.

There are many spraying methods, for example,

(1) spraying the slurry of the three components,
(2) respectively spraying the coating powder and organic bonding material dissolved in organic solvent,
(3) spraying in the sequence of organic solvent → organic bonding material → powder to be coated.

These methods are applicable. Usually it is the most uniformly mixed and, therefore, the most effective, that the three components are mixed before spraying. In this case, it is preferable for practical use that the slurry of the mixture is sprayed by side gas from the same nozzle as the mixture. Acrylic copolymer is preferable in terms of high bonding strength, ease of removal by heat treatment and no remainder after the removal. Other organic bonding materials are also applicable provided they are removable. It is possible for materials, such as plasticizer and lubricant at compression and materials to increase the pore ratio in the coated particle, to be added to the organic bonding materials in spite of no contribution to bonding strength, provided that these materials are removable. These organic materials are also described under the term organic bonding material in this invention. An organic solvent is required to have solubility of the organic bonding materials, dryability and security. Lower alcohols such as ethyl alcohol and iso-propanol (2-propanohol)are preferable when acrylic copolymer is used as organic bonding material. Inert gases such as nitrogen and argon are preferable as drying gas, but air is available. However, moisture in the air must be excluded since the solvent metal is sometimes oxidized by the moisture.

In the coated-with-sprayed-powder method, all of the supplied powder does not adhere to the core particles. Adherent ratio of the supplied powder sometimes depends on the kind and particle size of the powder. For example, the supplied mixture of 80:20 (weight ratio) of Ni:graphite became a composition of 75:25 (weight ratio) in coated layer. It is necessary to investigate the adherent ratio and the composition of the coated layer prior to the experiments. Particle diameter of the powder is preferably smaller than 1/10 of a core particle diameter. It is usual that the smaller diameter and lighter weight of the powder, the better adherence of the powder to the core particle.

The most preferable method is using Wurster type fluidizing bed in the coated with sprayed powder method. The seed crystals are cohered in other methods. That is coated particles randomly contain more than one seed crystal and such particles must be removed. On the other hand, such particles are seldom found when Wurster type fluidizing bed is used. Since the Wurster type fluidizing bed has an inner cylinder 14 as shown in Fig. 7 A or has a broader portion at the upper part as shown in Fig. 7 B, the particle decreases the velocity at the upper part and falls down along the outer cylinder 9. As the particles flow out in one direction and regularly circulate, cohesion rarely occurs. In the figure, (a) is the flow of slurry which contains powder to be coated/organic bonding material/organic solvent, (d) is the flow of drying gas and (f) is the flow of core particles.

Next the producing methods of coMPacts are explained.

Before going in to detail, the organic bonding material must necessarily be removed by heat treatment before or after compaction. Especially when the organic bonding material is included excessively, most of it should be removed before compaction. When it is removed after coMPaction, the filled amount in the diamond synthesized vessel decreases since a pore remains in a compact. The removal temperature depends on the kind of organic bonding material and is about 300~600°C. Of course, the heat treatment should be carried out in a reduced or an inert atmosphere in order to prevent oxidation.

Since a small amount of organic lubricant contribute to high density of a compact at compaction, and, therefore, is advisable that an organic bonding material include an amount of organic lubricant in which removing temperature is higher than the organic bonding material.In this case, most of the organic material is removed at comparatively low temperature and compacting and then a small amount of the remainder (organic lubricant) is removed at coMParatively high temperature. Using the mixture of acrylic copolymer whose removing temperature is about 400°C and a small amount of organic lubricant whose removing temperature is about 500 ~600°C, the density of the compact increases after the processes of heat treatment at 400°C and compacting and then heat treatment at 600°C. In order to increase the strength of the compact, treating at higher than 600°C is considered. A reduced atmosphere is suggested since solvent metal is reduced.

It is important at compaction molding that all directions of distances between synthesized diamond particles are as uniform as possible at the end of synthesizing.

When the direction of the distances differs from other directions, the shortest distance should be of adequate distance to not disturb each other. Therefore, the number of filled seed crystals decreases, resulting in the decrease in yield of diamond as well. Since this phenomenon relates to ultra-high pressure apparatus, properties of each apparatus are explained hereafter respectively.

The first, a one-axis ultra-high pressure apparatus is explained in Fig. 10A, which is used widely in industry. The synthesized vessel of this apparatus is usually a circular column, so a compact is basically molded into a circular column. Considering the most general compaction molding in the direction of circular column axis using a metal die, the distance between seed crystals is the same as the size of a coated particle in radial direction, but decreases in proportion to compacted length in axial direction. Furthermore, the following phenomena occur in the ultra-high pressure apparatus.

(1) Since synthesized space spreads in the radial direction, and lessens in proportion to the spread in the axial direction, the distance between the seed crystals increases in the radial direction and further shrinks in the axial direction.
(2) There is no pore under the ultra-high pressure condition. Volume of a compact decreases in proportion to the remaining pore in the compact; the decrease causes the shortening of distance between seed crystals in the axial direction.
(3) Volume of raw carbon decreases accompanied by the transformation of non-diamond carbon to diamond; the decrease also causes the shortening of distance between seed crystals in the axial direction.

It is, therefore, found in the arrangement of the compact that the distance between the seed crystals in radial direction is relatively shorter than in the axial direction as shown in Fig. 4. The present inventors have succeeded in using a dry-cold-isostatic-press apparatus or a method of pseudo-dry-cold-isostatic-press with a wet-cold-isostatic-press apparatus. The compact is uniformly compacted from all directions, as shown in Fig. 8A in normal use of a wet-cold-isostatic-press apparatus which is widely used as an apparatus of cold-isostatic-press. On the other hand, the compact is pressed only from the radial direction with a dry-cold-isostatic-press apparatus as shown in Fig.8B. When the wet-cold-isostatic-press apparatus is used with a supporting case having side holes which controls pressing in the axial direction by side pores as shown in Fig.9A, the apparatus has the same properties as the dry-cold-isostatic-press apparatus (this is defined as "pseudo-dry-cold-isostatic-press).

Compaction ratio of a radial direction and an axial direction, namely, distance ratio of seed crystal, can be controlled by pore ratio in coated particle and filled ratio in a compaction mold. The pore ratio has an especially important role on the compaction ratio and can be controlled by the amount of organic bonding material as mentioned before. The volume of organic bonding material is considered to be pore in the coated particles when the coated particles are dewaxed before compaction. It is carried out by increasing the amount of organic bonding material that is intended for compaction in the radial direction. In many cases, adequate distance ratio of seed crystal can be obtained by controlling the size and pore ratio of coated particle and using the dry or pseudo-dry-cold-isostatic-press.

It is sometimes necessary to compact a little in the axial direction. In this case, the following methods can be used.

(1) Using a dry-cold-isostatic-press apparatus which has the ability to compact and control in the axial direction.
(2) Using a pseudo-dry-cold-isostatic-press apparatus with supporting case in which a compact is compacted a little in the axial direction as shown in Fig. 9B.
(3) Before or after compaction of coated particle using a dry-cold-isostatic-press, the coated particle is compacted in the axial direction using a metal die or a wet-cold-isostatic-press apparatus.

In the next case of using multi-axes ultra-high-pressure apparatus as shown in Fig. 10B, since a compact is shrinked almost uniformaly from all direction, it is preferable that the distance between seed crystals in a compact is uniform. Such compact can be obtained easily by using a wet-cold-isostatic-press apparatus.

In Figs. 8, 9 and 10,16 stands for particles to be compacted, 17 stands for rubber molding, 18 stands for liquid pressure medium, 19 stands for steel vessel, 20 stands for a metal lid, 21 stands for supporting case. 22 stands for synthesizing vessel of diamond, 23 stand for die made of cemented carbide 24 stands for anvil made of cemented carbide, 25 stands for ceramic pressure medium, 26 stands for electro conductive parts, 27 stands for graphite heater. (g) stands for a compacting direction in a cold-isostatic-press apparatus and (h) stands for a compacting direction in a ultra-high-pressure apparatus.

Using only the compact 15 which is obtained by the above methods, high strength diamond particles can be effectively synthesized with any prior method or the new method.

The multilayer method can be applicable to synthesize diamond particles using these coated particles. In other words, the method uses single layer compact of coated particles with raw carbon plate and solvent metal plate as shown in Fig. 5A. There is no advantage in stacking only the single layer compact compared with using a circular column compact. The single layer compact is preferably combined with raw carbon and/or solvent metal layer as shown in Fig. 5B. In this case, the distance between the seed crystals in thickness direction is kept and controlled by the plate of raw carbon 7 and / or solvent metal 6. Therefore, the amount of coated raw carbon and solvent metal should be maintained to have sufficient distance between seed crystals in the single layer. It is preferable the simplest to make a single layer compact with a metal die. When compacting the coated particles, the following method is suggested in handling the single layer compact. The plate of raw carbon or solvent metal is coated with organic adhesive and the coated particles are arranged and adhered to the plate and then the combination is compacted as it is. Needless to say, the organic adhesive and organic bonding material should be removed by heat treatment prior to synthesizing diamond.

Comparing with the conventional multilayer method, especially seed crystals arranged orderly in a layer, this invention is advantageous in that the seed crystals do not move under even the condition of synthesizing diamond, because each seed crystal is surrounded by solid raw carbon. Synthesized diamond particles have remarkable strength compared with the conventional method. Since the amount of yield is the same as the conventional multilayer method, it is suggested that the above invented compact be used in the multilayer method. Such method, therefore, has high industrial applicability because the coating amount can decrease, a small amount of coated diamond particles is used and isostatic-press apparatus is not needed.

As explained above, diamond which is produced by using invented coated particle, has a small lack portion, good symmetry and high strength. Therefore the diamond is applicable to not only abrasive sawing but also to a diamond wheel and a dresser.

The method of producing the coated particle is preferable to industrial use, because composition, particle size and pore ratio of a coated layer are controlled by selected fine diamond particle and powder to be coated.

It is possible to synthesize a diamond, only putting the coated particle or the mixture of the coated particle and other raw materials into the synthesizing vessel for diamond in ultra-high pressure apparatus. However, when the coated particle or the mixture of the coated particle and other raw materials is compacted previously, and then synthesized to diamond, the amount of diamond yield and quality are remarkably improved .

Example 1.

Single crystal diamond particles having the size of 325/400 mesh were coated with sprayed slurry which consisted of raw carbon/solvent metal/organic bonding material/organic solvent, using the apparatus shown in Fig. 7A. The raw carbon was graphite powder, solvent metal had the composition of, Fe:Ni=58:42(weight ratio), organic bonding materials were acrylic copolymer and polyethylene glycol, and organic solvent was isopropanol. The mixed ratio was (graphite) : (Fe-Ni alloy) : (acrylic copolymer) : (polyethyleneglycol) : (isopropanol)=25:75:7.5:7.5:125(by weight ratio). Heated air of 80°C was used as dry gas. Measuring the diameter of the coated particles which were intermittently picked out from the apparatus, the coating was stopped when the coated particles became about 800 μm diameter. The coated layer had the composition of (graphite):(Fe-Ni alloy) =28:72(weight ratio). Coated particles having 750~810 μm diameter were obtained by sieving and organic bonding material was removed in hydrogen stream at 450°C for 60 minutes. The particles were compacted into a circular column under a pressure of 3000kgf/cm^2 (294MPa) applying the case as shown in Fig. 9A to the apparatus of Fig. 8 A. The circular column compact was cut and pressed in a metal die under a pressure of 6000kgf/cm^2 (588MPa)in the axial direction and then heated in hydrogen stream at 1000°C for 60 minutes. The apparent density of the compact was 85% of theoretical density. The compact was worked into a circular column of 25mm diameter and 20mm height, and then the circular column was put into a one-axis ultra-high pressure apparatus as shown in Fig. 10A. The compact was exposed to the condition of 5.3 GPa and 1350°C for 30 minutes, and diamond particles were obtained.

The yielded amount of diamond particles was 7.6 grams and particles of 5.2 grams out of 7.2 grams had a size of 40/50 mesh. Particles of 4.4 grams out of 5.2 grams had no lack portion, good symmetry and high strength. The measuring method of strength and comparative examples are summarized after the examples.

Example 2.

Single crystal diamond particles having the size of 230/270 mesh were coated with raw carbon/solvent metal using the apparatus shown in Fig. 6B. Dry gas stirred the particles to a certain extent, because the horizontall rotating disk 12 was porous plate. The mixture of raw carbon powder/solvent metal powder and organic solvent dissolving organic bonding material were alternately sprayed from nozzles 10 and 13. The raw carbon was graphite powder and solvent metals was a mixture of Fe powder and Co powder. Composition of the mixture was (graphite) : Fe :Co =40:30:30 (weight ratio). Organic bonding materials were acrylic copolymer and ethyl cellulose, and organic solvent was ethanol. Acrylic copolymer and ethyl cellulose in the ethanol was 10 wt% and 2wt%. Nitrogen gas of 50°C was used as dry gas.

Measuring the diameter of coated particles which were intermittently extracted from the apparatus, the coating was stopped when the coated particles became about 1000 µm. Coated particles having 960~1060 µm diameter were heated to remove the organic bonding material as described in Example 1 and then the coated particles were coMPacted into a circular column compact under a pressure of 4000kgf/cm^2 (392MPa) using the method shown in Fig. 9A. This coMPact was heated, and worked as described in Example 1. The apparent density of the compact was 87% of theoretical density.

The compact was exposed for 45 minutes using the same apparatus under the same condition as Example 1. The amount of yielded diamond was 6.4 grams, and 4.2 grams out of 6.4 grams had a size of 30/40 mesh. Particles of 3.2 grams were high strength diamond.

Example 3

Single crystal diamond particles having the size of 325/400 mesh were coated using the same apparatus and the same method as described in Example 1. But the composition of the slurry was (graphite):(Fe-Ni alloy):(acrylic copolymer):(polyethylene glycol) : (isopropanol)=5:95:5:5:75 (weight ratio). After the particles were coated aiming at 600 µm diameter, particles having 540~600 µm in diameter were selected. These particles were heated at 400°C for 30 minutes in hydrogen stream to remove the organic bonding material, and then mixed with graphite powder. The mixture ratio was (coated particles):(graphite powder) =70:30 (weight ratio)=39:61(volume ratio). A compact was obtained in the same manner as described in Example 2 and the apparent density of the compact after heat treatment and working was 89% of theoretical density. Diamond was synthesized in the same manner as described in Example 1, the amount of yielded diamond was 7.8 grams and 4.8 grams out of 7.8 grams had a size of 40/50 mesh. Particles of 3.4 grams was high strength diamond.

Example 4.

Single crystal diamond particles having the size of 140/170 mesh were plated with Co by electroless plating, and grew to about 150 µm in diameter. The coated particles were further coated with only carbon powder in the same manner as described in Example 2 so that the coated composition became Co:graphite=75:25(weight ratio). After the coated particles were compacted into a circular column compact under a pressure of 3000kgf/cm^2 (294MPa) applying the case as shown in Fig. 9A to the apparatus of Fig. 8 A, the compact was heated at 1050°C in hydrogen stream for 30 minutes. The apparent density of the compact was 82% of theoretical density. The compact was worked into the same size circular column as Example 1 and exposed to the condition as described in Example 1 for 15 minutes. The amount of yielded diamond was 7.3 grams and 5.4 grams out of 7.3 grams had a size of 50/60 mesh , and 4.8 grams out of 5.4 grams was high-strength particles.

Example 5.

Coated particles were produced as described in Example 1. The coating was stopped at a little smaller than 500 µm in diameter. Particles having 425~500 µm diameter were selected and heated at 450°C in hydrogen stream for 60 minutes to remove organic bonding material.

The particles were arranged in a mono-layer with the most close-packed in a one-axis compacting die, and compacted into plate compact of 22mm diameter and 135 µm thickness under the pressure of 2000kgf/cm^2 (196MPa). A 58 wt% Fe-42 wt% Ni alloy plate having 22mm diameter and 100 µm thickness and a graphite plate of 22mm diameter and 400 µm thickness were prepared. These plates were combined in the order of (Fe-Ni alloy plate)/(plate compact)/(Fe-Ni alloy plate)/(graphite plate) as shown in Fig. 5B. It was exposed to the same conditions as Example 1 to synthesize diamond in that the multilayer plates were composed of the number of 20 compact plates, the number of 40 Fe-Ni alloy plates and the number of 21 graphite plates. The amount of yielded diamond was 3.6 grams and 2.4 grams out of 3.6 grams had a size of 40/50 mesh, and 2.0 grams out of 2.4 grams was high strength particles.

Example 6.

Single crystal diamond particles having the size of 325/400 mesh were coated by the same apparatus and in the same manner as described in Example 1. But the composition of the slurry was (graphite) : (Fe-Ni alloy) : (wax) : (ethanol)=30:70:3:100(weight ratio). After the particles were coated aiming at 2mm diameter, particles having 1.7~2.4mm diameter were selected and heated at 550°C in hydrogen stream for 60 minutes to remove the organic bonding material. The particles were then compacted into a circular column compact under the pressure of 3000kgf/cm^2(294MPa) applying the case as shown in Fig. 9A to the apparatus of Fig. 8 A. The compact was heated at 1100°C in hydrogen for 60 minutes, and then worked as described in Example 1. The apparent density of the compact was 86% of theretical density. The compact was exposed under the conditions described in Example 1, but the keeping time was 60 minutes to synthesize diamond. The amount of yielded diamond particles were 6.0 grams and 3.4 grams out of 6.0 grams were a size of 20/25 mesh, and 1.9 grams out of 3.4 grams were high strength particles.

Example 7.

Single crystal diamond particles having 20~30 µm diameter were coated by the same apparatus and the same manner as described in Example 1. But the composition of the slurry was Fe:Ni:(acrylic copolymer):(isopropanol)=70:30:3:70(weight ratio), and dry air was 70°C. After the particles were coated aiming at 50 µm in diameter, the particles having 44~63 µm in diameter were selected. These particles were further coated by the same apparatus and the same manner as described in Example 1. The composition of the slurry was(graphite):(Fe-Ni alloy):(acrylic copolymer):(maleic anhydride ester) : (isopropanol)=25:75:5:6.5:95(weight ratio).

After the particles were coated aiming at 800 µm in diameter, the particles having 710~840 µm in diameter were selected and heated at 600°C in mixed gas of 10vol% hydrogen and 90vol% nitrogen for 30 minutes to remove the organic bonding material. These particles were molded into a circular column compact under the pressure of 2500kgf/cm^2 (245MPa)as the same manner as Example 6. The compact was heated at 1100°C in 100 torr of reduced pressure of hydrogen for 60 minutes, and then worked as described in Example 1. The apparent density of the compact was 83% of theoretical density. Diamond particles were synthesized as described in Example 1. The amount of yielded diamond particle were 7.2 grams, 4.9 grams of which were a size of 40/50 mesh and 3.9 grams out of 4.9 grams were high strength diamond particles. But the inclusions around the seed crystals were remarkably reduced compared with Example 1.

Example 8.

Single crystal diamond particles which were plated with Cu in 50 weight %and had 22~36 µm in diameter, were coated by the same apparatus and the same manner as described in Example 1. But the composition of the slurry was Fe:Ni:(acrylic copolymer) : (maleic anhydride ester) : (isopropanol) =70:30:1:2.5:70(weight ratio), and drying air was 70°C.

After the particles were coated aiming at 50 µm in diameter, the particles having 44~63 µm in diameter were selected. These particles were further coated by the same apparatus and the same manner as described in Example 1. The composition of the slurry was (Fe-Ni alloy):(acrylic copolymer):(maleic anhydride ester) : (isopropanol) =100:1:2.5:70(weight ratio).

After the particles were coated aiming at 200 µm in diameter, the particles having 180~210 µm in diameter were selected. These particles were further coated by the same apparatus and the same manner as described in Example 1. The composition of the slurry was (graphite):(Fe-Ni alloy):(acrylic copolymer):(maleic anhydride ester):(isopropanol)=25:75:2:5:95(weight ratio).

After the particles were coated aiming at 800 µm in diameter, the particles having 180~210 µm in diameter were selected. The following steps such as removing organic bonding material, compaction, heat treatment, working and synthesizing diamond, were carried out as described in Example 6. The amount of yielded diamond particles was 7.5 grams and 5.1 grams out of 7.9 grams were a size of 40/50 mesh and 4.4 grams out of 5.1 grams were high strength particles. The inclusions around the seed crystals were remarkably reduced and appeared to reduce beyond Example 7.

Example 9.

Single crystal diamond particles which were plated with Ni in 56 weight % and had 30~40 µm in diameter, were coated by the same apparatus and the same manner as described in Example 2. But (1) the slurry of (solvent metal)/(organic bonding material) was sprayed in the direction of tangential line of the outer cylinder of the coating equipment, (2) the composition of slurry was Fe:Ni:(acrylic copolymer):(isopropanol)=70:30:3:70(weight ratio), and dry air was the temperature of 60°C.

After the particles were coated aiming at 50 µm in diameter, the particles having 44~63 µm in diameter were selected. These particles were further coated by the same apparatus and the same manner as described in this Example 2. The composition of the slurry was Fe:Ni:(graphite):(acrylic copolymer) : (isopropanol) =49:21:30:3:70(weight ratio).

After the particles were coated aiming at 800 µm in diameter, the particles having 710~840 µm in diameter were selected. The following steps such as removing organic bonding material, coMPaction, heat treatment, working and synthesizing diamond, were carried out as described in Example 6. The amount of yielded diamond particles was 7.5 grams, 4.9 grams of which were a size of 40/50 mesh and 4.1 grams out of 4.9 grams were high strength diamond particles. The inclusion around the seed crystals appears to be the same extent as Example 8.

It is explained in each Example that the amount of yielded diamond particles were A gram, B gram out of A gram particles have a size of C and D gram out of B gram were high strength diamond particles. The estimation was based on the pot-mill method which is widely used in the diamond tool field.

The method is explained hereafter on the assumption that the object of diamond particles is a size of 40/50 mesh and approximately the same size of diamond particles are manufactured. The amount of A gram of manufactured diamond particles are sieved and B gram of a size of 40/50 mesh is obtained. Examples 1, 3, 5, 7, 8 and 9 correspond to this assumption. The following amount of diamond particles out of B gram in each example are put into the steel capsule (31) for measuring impact strength as shown in Fig. 14, and shaked with a steel ball (32) under the following condition.

inner volume of the capsule	about 2.5CC
diameter of steel ball	5/16 inch
number of steel ball	1
revolutions of steel capsule	2400rpm
amplitude of vibration	about 8 mm
shaking time	about 50 second
amount of diamond	2ct(0.4g)

The shaked diamond particles are removed from the capsule and sieved by estimation sieve of 302 µm. Weight % of the amount under the estimation sieve is the crushed ratio and this % is called crushability. On the other hand, weight % of the amount over the estimation sieve is called strength or toughness. The strength of each above example is shown in Table 1 and is stronger than comparative Example which is put on the market. The meaning of "after heat treatment" is that the value is measured at room temperature after heat treatment of 1100°C × 30 minutes in vacuum.

Table 1

	Particle Diameter	Estimation Sieve	Toughness(%)	
			No Heat Treatment	After Heat Treatment
Example 1	#40/50 (300~425 µm)	302 µm	84	79
Example 3	#40/50 (300~425 µm)	302 µm	81	78
Example 5	#40/50 (300~425 µm)	302 µm	82	77
Example 7	#40/50 (300~425 µm)	302 µm	84	82
Example 8	#40/50 (300~425 µm)	302 µm	85	84
Example 9	#40/50 (300~425 µm)	302 µm	84	81
CoMParative Example 1	#40/50 Popular Grade on Market	302 µm	70-75	60-70
CoMParative Example 2	#40/50 High Grade on Market	302 µm	75-80	70-77
CoMParative Example 3	#40/50 Highest Grade on Market	302 µm	85	83

Claims

1. A particle for synthesizing diamond comprises: a single crystal of fine diamond particle being coated with at least one layer which contains at least one kind of solvent metal powder for synthesizing diamond and/or at least one kind of solvent metal powder with organic bonding material.

2. A particle for synthesizing diamond according to claim 1, wherein said layer contains non-diamond carbon.

3. A particle for synthesizing diamond according to claim 1 or 2, wherein the organic bonding material contains acrylic copolymer.

4. A process for synthesizing diamond comprises these steps: coating fine diamond particles with at least one layer which contains at least one kind of solvent metal powder for synthesizing diamond and/or at least one kind of solvent metal powder with organic bonding material, filling a molding with said coated fine diamond particles, compacting, arranging a compact in a synthesizing vessel, heating said compact to a temperature above the solvent metal-graphite melting point with a pressure condition in which diamond is thermodynamically stable, and recovering said diamond abrasive particles.

5. A process according to claim 4, in which said layer contains non-diamond carbon.

6. A process according to claim 4 or 5, in which said organic bonding material contains acrylic polymer.

7. A process according to any of claims 4 to 6, in which said coating is carried out by spraying method.

8. A process according to any of claims 4 to 7, in which said coated particles are further coated with a mixture of at least one material selected from a solvent metal powder, a non-diamond carbon, an organic bonding material and an organic solvent.

9. A process according to any of claims 4 to 8, in which said coating is carried out using Wurster type fluidized bed or horizontally rotating disk equipment.

10. A process according to any of claims 4 to 9, in which said coated diamond particles are heated at about 300~600°C to remove an organic bonding material.

11. A process according to any of claims 4 to 10, in which said compact is heated to about 300~600°C to remove an organic bonding material.

12. A process according to claim 10 or 11, in which heating is carried out in a reduced or an inert atmosphere.

13. A process according to any of claims 4 to 12, in which said compaction is carried out using cold-isostatic press.

14. A process according to claim 13, in which said cold-isostatic press is carried out by a pseudo-dry-cold isostatic press using a wet-cold isostatic press or dry-cold-isostatic press.

15. A process according to any of claims 4 to 14, in which said compact is a mono-layer of coated particles.

16. A process according to any of claims 4 to 15, in which said compact is stacked with non-diamond carbon plate and/or solvent metal plate in a synthesizing vessel.

Fig. 1

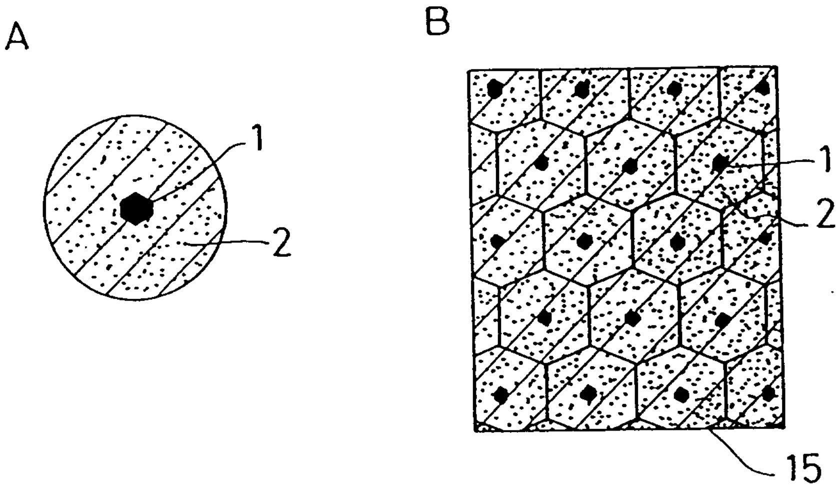


Fig. 2

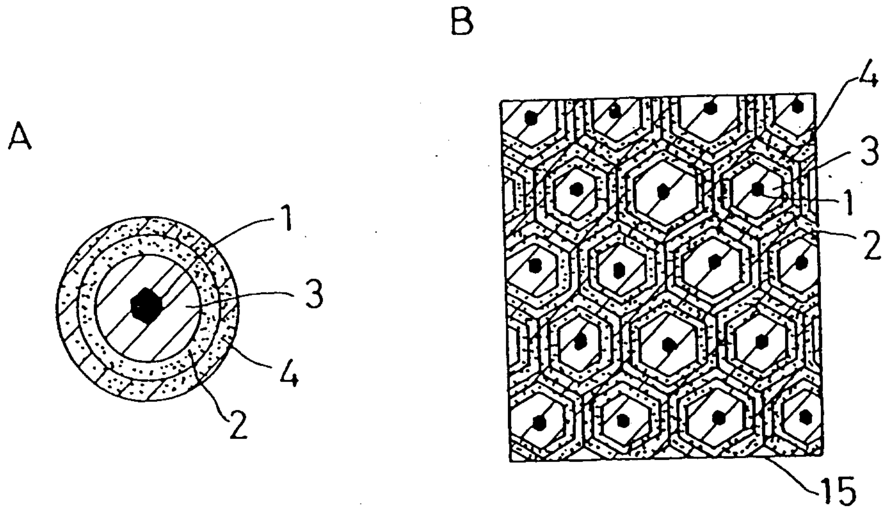


Fig. 3

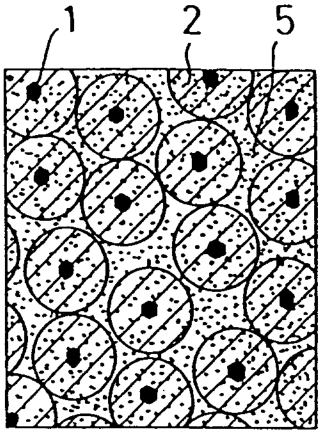


Fig. 4

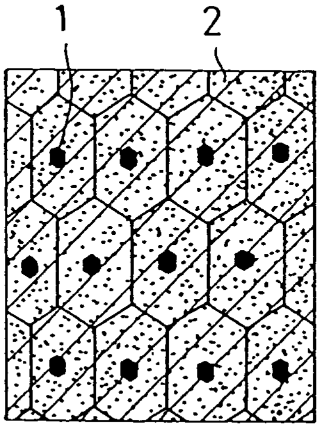


Fig. 5

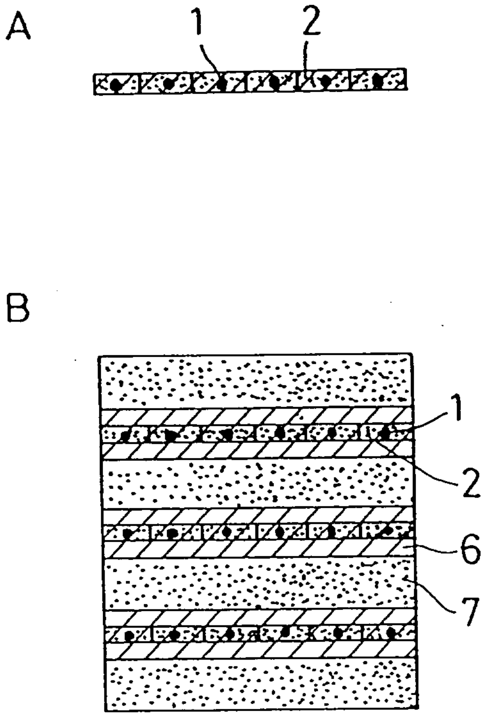


Fig. 6

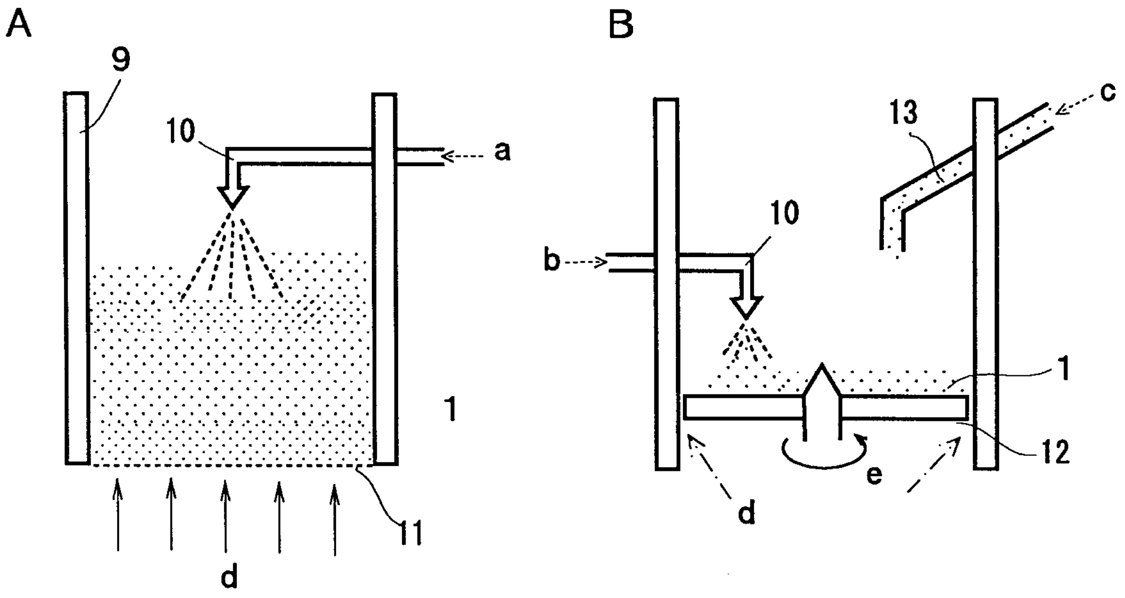


Fig. 7

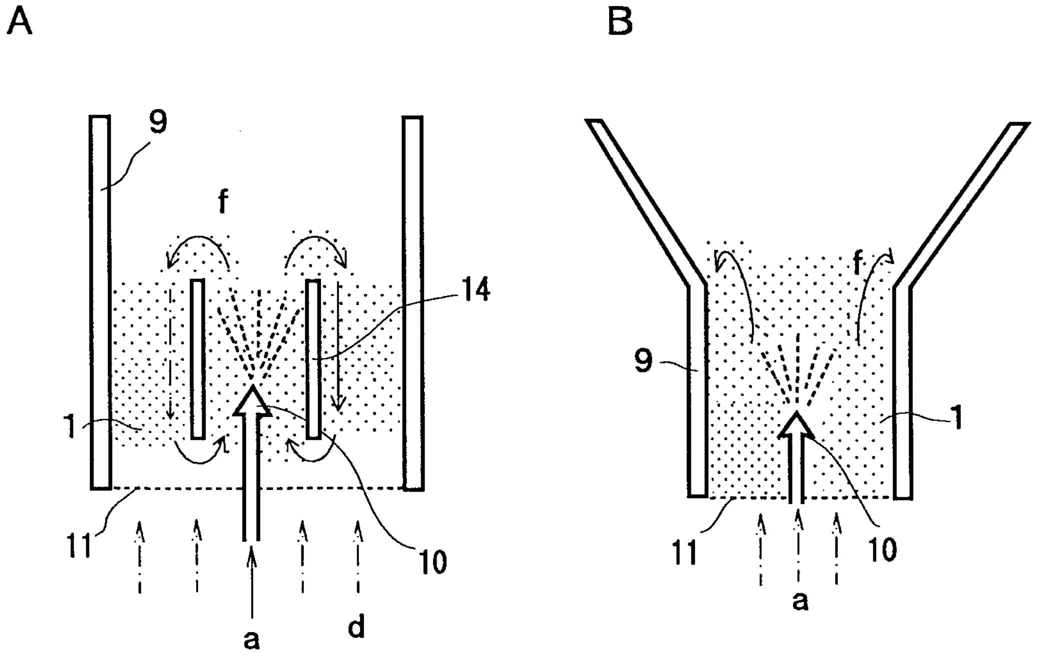


Fig. 8

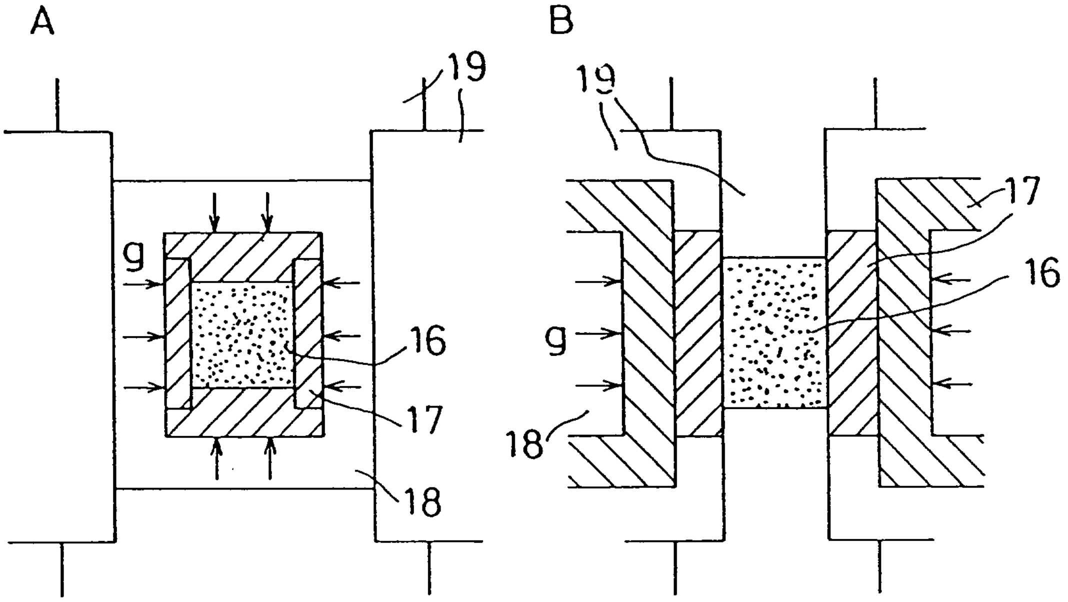


Fig. 9

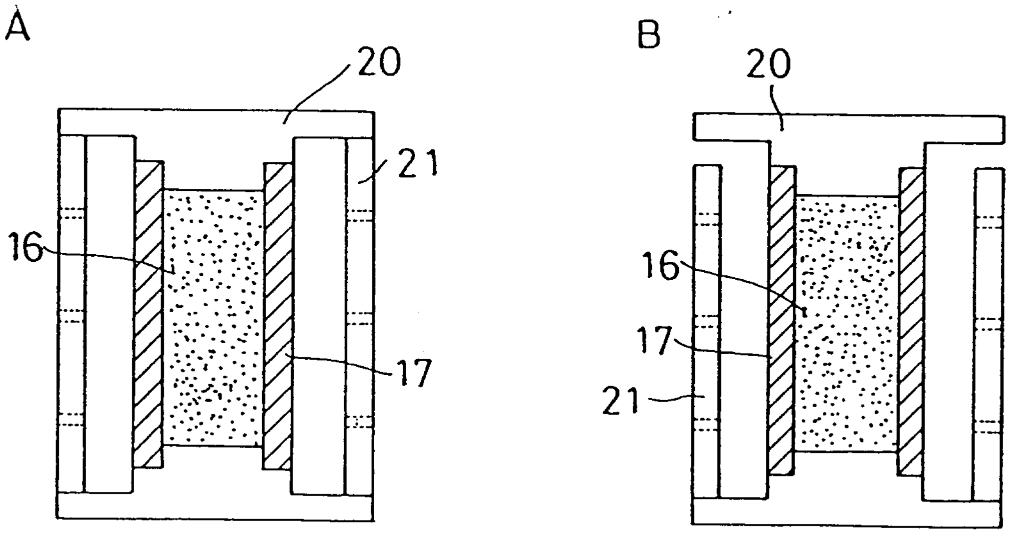


Fig.10

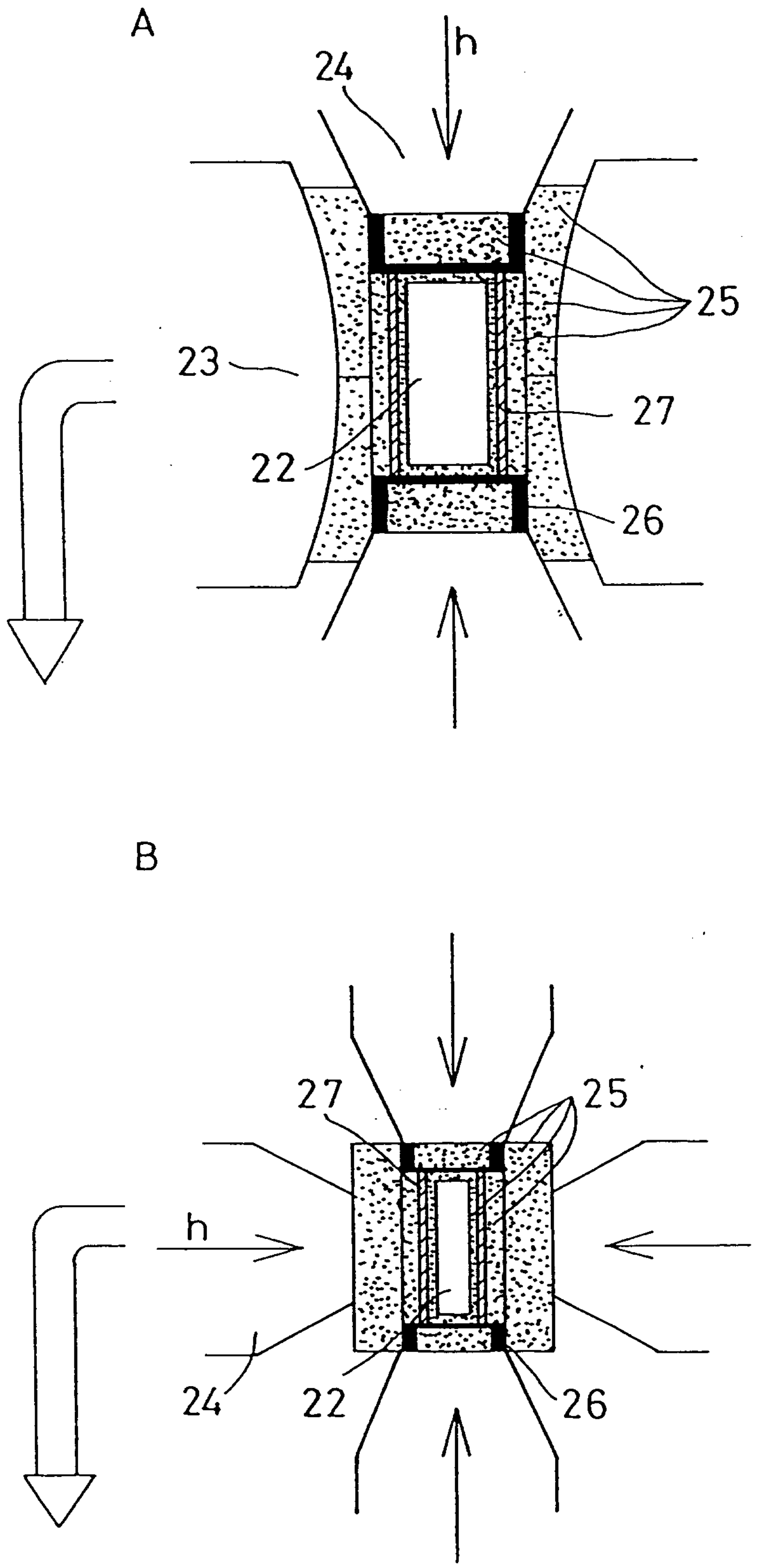


Fig.11

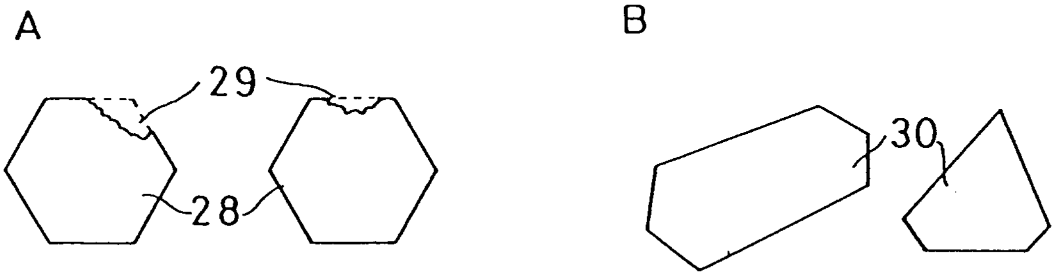


Fig.12

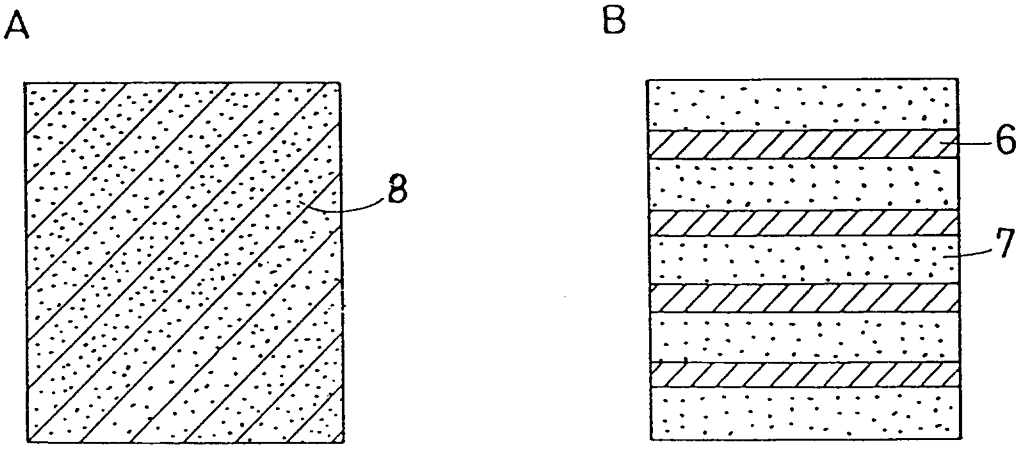


Fig. 13

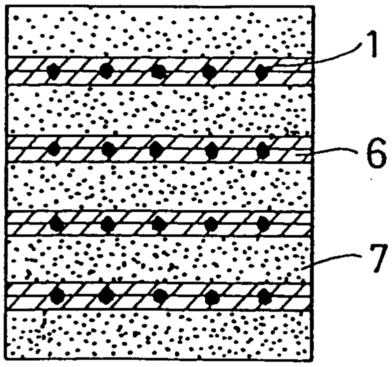


Fig. 14